



The electrochemical performances of a novel lead–sodium binary grid alloy for lead-acid batteries

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ABSTRACT

A series of Pb–Na alloys were synthesized by adding sodium to lead. Linear sweep voltammetry (LSV), cyclic voltammograms (CV), electrochemical impedance spectroscopy (EIS), open circuit potential (OCP), and other analytical methods were used to investigate the electrochemical performances of the Pb–Na alloys in 1.28 g cm^{−3} H₂SO₄ solution. The results indicate that the addition of sodium reduces the generation of PbO and PbSO₄ greatly during anodic process, inhibits the oxygen evolution reaction and accelerates the evolution of hydrogen, and the Pb–Na alloys have good cycle performance and corrosion resistance properties. The alloys retain the merits, whilst removing the flaws, of the pure grid, thereby providing a promising positive grid alloy for spirally wound lead acid batteries.

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1. Introduction

In the short to medium term, hybrid electric vehicles are generally regarded as having the greatest potential for improving air quality [1]. The lead-acid battery system still serves as the most suitable power source because it offers several advantages over other advanced battery systems, including: availability, low cost, satisfactory power density, safety and an established infrastructure for battery manufacturing and recycling [2]. Compared to the conventional flat-plate configuration, the spirally wound construction for VRLA cells provides the following advantages: a uniformly high plate compression to extend the cycle life; the use of comparatively thin plates to improve the specific power; the use of pure lead or soft lead alloys to reduce gassing; simpler, cost-competitive manufacturing techniques.

During the past two decades, lead-acid batteries have been applied in automobile, solar energy storage, and emergency lighting systems, etc. To improve the corrosion resistance, gassing overpotential, rate capability, and cycle performance of lead-acid

batteries, recent grid alloy research for VRLA cells has focused on low-antimony and lead–calcium grid alloys. Sb can dissolve and deposit on the negative electrode, causing hydrogen evolution, followed by water loss. Also, whereas a Pb–Sb grid requires less maintenance, it is not maintenance-free. With a high overpotential for hydrogen evolution, Pb–Ca grids have been applied in lead-acid batteries; to overcome calcium loss and improve casting performance, manufacturers produced Pb–Ca–Sn–Al grids, and researchers are developing new additives for Pb or Pb–Ca grids [3–12]. Whereas a Pb grid has good casting and float charge performance, and hence is used in spirally wound VRLA batteries, it does not have a satisfactory deep cycle capacity due to a corrosion layer formed between the grid and the active material [13].

For this study, a series of novel grid alloys were prepared by the addition of Na to Pb; their electrochemical performance and decay resistance were then investigated. Experimental results demonstrate that these grid alloys have very high oxygen evolution potential, thus the addition of sodium inhibits oxygen evolution, plus enhances corrosion resistance, and provides a new positive grid alloy for spirally wound lead acid batteries.

2. Experimental

Electrolytic lead (99.994%) and pure metallic sodium (A.R.) were used as raw materials. A batch of lead and metal sodium packed

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in rolled lead (typically 10 kg lead with 2, 6 or 10 g sodium) were melted under an argon gas atmosphere in an electrical furnace at 400 °C for 10 min, then cooled down to 350 °C, and maintained under these conditions for 1 h to form a homogeneous Pb–Na alloy. The alloy was then cast into a cylindrical mould, which was held in a muffle furnace at 300 °C for 1 h, before being cooled to room temperature in order to be prepared as working electrodes. The cylindrical alloys were approximately 8.0 mm in diameter and 16 mm in length. There was some burn spoilage of sodium. The purity of the sodium was determined using an iCAP6500 (Thermo-Electron Corporation) inductive coupled plasma emission spectrometer (ICP), and were found to be 0.01%, 0.05% and 0.08%. Finally, the pure Pb, Pb–0.01 wt.% Na, Pb–0.05 wt.% Na and Pb–0.08 wt.% Na alloys, numbered as 0#, 1#, 2#, 3# respectively, were selected and used as the working electrodes for electrochemical studies.

For electrochemical measurements, a three-electrode conventional glass cell was used. A copper wire was welded to the top of the cylindrical alloy to form a working electrode, then sealed with epoxy resin to avoid any contact with the electrolyte solution, leaving only the lower ($\pi \times 0.4^2 \text{ cm}^2$ surface area) end face exposed. Prior to each experiment, all working electrodes were mechanically polished with 800-, 1500- and 2000-grade SiC emery paper, then cleaned with absolute ethyl alcohol to remove oil contamination on the surface, followed by double-distilled water. The counter and reference electrodes were a platinum plate (0.3 cm² surface area) and a Hg/Hg₂SO₄ electrode (1.28 g cm⁻³ H₂SO₄ solution, $E = +0.658$ vs. SHE), respectively. All potentials are reported with respect to this reference electrode. The three electrodes were inserted vertically into a 1.28 g cm⁻³ H₂SO₄ solution, which was prepared from analytical grade reagent and maintained at 25 °C. Prior to each experiment, a cathodic potential of -1.2 V was applied for 20 min to reduce any oxide formed during pre-treatment. Electrochemical impedance spectroscopy (EIS), open circuit potential (OCP), cyclic voltammetry (CV), and linear sweep voltammetry (LSV) were used to investigate the effects of sodium content on the electrochemical behavior of lead–sodium alloys in sulfuric acid solution. The electrochemical measurements were conducted on an Autolab PGSTAT-30 potentiationstat/galvanostat (ECO Echemie B.V., Holland). For the EIS measurement, a single wave with 5 mV amplitude from 100 kHz to 0.01 Hz was utilized.

3. Results and discussions

3.1. Electrochemical impedance spectroscopy

A sample Nyquist plot, obtained on Pb and Pb–Na alloys with a potential of 1.5 V, after oxidation at 1.5 V for 1 h is presented in Fig. 1.

The EIS data reveal that each impedance diagram consists of a semicircle, indicating a single time constant for the process, thus it is proposed that the oxygen evolution at 1.5 V is controlled by a charge transfer process at the metal/oxide film interface.

The data were approximated using a variety of electronic equivalent circuits; the best fit was provided by the equivalent circuit sketched in Fig. 2, in which R_s denotes the solution resistance, R_{ct} represents the charge transfer resistance for oxygen evolution at 1.5 V, and C is the capacitance.

The R_s , R_{ct} , and C values are listed in Table 1.

The resistance for oxygen evolution, R_{ct} , increases with alloy sodium content, indicating that the rate of oxygen evolution was reduced in the presence of Na, consistent with the preceding experimental results.

The R_s values of 2#, 3# alloys are smaller than that of Pb. It can be concluded that the addition of sodium reduces the solution resis-

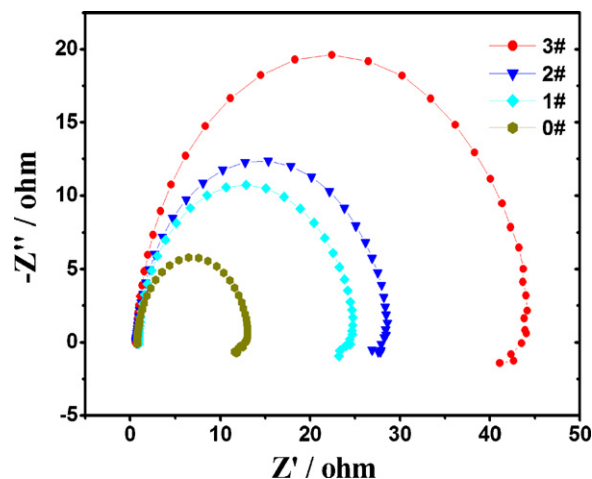


Fig. 1. The Nyquist plot obtained for the 0#, 1#, 2#, and 3# electrodes at a potential of 1.5 V in 1.28 g cm⁻³ H₂SO₄ solution, following oxidation at 1.5 V for 1 h.

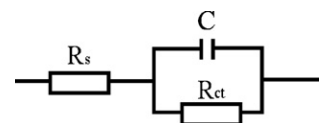


Fig. 2. The electrical equivalent circuit used to fit the impedance data (Fig. 1) of each electrode.

tance, possibly because some sodium can dissolve into the H₂SO₄ solution, thereby accelerating electron transfer.

3.2. Linear sweep voltammetry

The electrodes were anodized at 1.3 V for 1 h, as 1.3 V is the float charge potential; the electrode potential was then swept to -1.2 V at a scan rate of 1 mV s⁻¹, yielding the voltammograms presented in Fig. 3.

In Fig. 3, peak 1 corresponds to Pb(IV) (representing the oxide formed on the surface of each electrode, including α -PbO₂ and β -PbO₂) being reduced to PbSO₄ or PbO, peak 2 results from the reduction of PbO to Pb, peak 3 from the reduction of PbO·PbSO₄ and PbSO₄ to Pb. The peak currents and peak potentials (I_p and E_p) are provided in Table 2.

It can be seen from peak 1 that all the Pb(IV) reduction peak currents of Pb–Na alloys are approximately half that of Pb, implying that the quantity of Pb(IV) generated on Pb–Na alloys is lower, and the same conclusion can be determined from peaks 2 and 3. The E_p values of Pb–Na at peaks 1 and 3 are lower than that of Pb, yet the E_p values of Pb–Na at peak 2 are higher than that of Pb, which implies that the reduction of PbO₂ to PbSO₄ or PbO, and PbSO₄ to Pb are more difficult, whereas PbO, PbO·PbSO₄ to Pb are easier, with the addition of sodium.

It can be concluded that the addition of sodium can decrease the generation of Pb(IV) and Pb(II), plus enhance the corrosion resistance of lead alloys and reduce grid expansion; the inhibitory effect of Pb–0.08%Na is the strongest.

Table 1
The parametric values of the equivalent circuit diagram.

Electrode	R_s (Ω)	R_{ct} (Ω)	C (mF)
0#	0.780	12.000	2.935
1#	0.885	22.860	2.387
2#	0.702	26.530	2.368
3#	0.647	41.600	1.620

Table 2

The variation of peak current (A), peak potential (V), and the reduction charges at peak1 ($Q_c/\text{mC cm}^{-2}$) with alloy sodium content from linear sweep voltammograms.

Electrode		0#	1#	2#	3#
Peak 1	E_p/V	1.037	1.023	1.025	1.024
	I_p/A	0.001190	0.000550	0.000300	0.000322
Peak 2	E_p/V	−0.959	−0.911	−0.919	−0.916
	I_p/A	0.001670	0.000550	0.000670	0.000499
Peak 3	E_p/V	−1.043	−1.051	−1.052	−1.052
	I_p/A	0.001450	0.000920	0.000750	0.000583
Q_c of peak 1	($Q_c/\text{mC cm}^{-2}$)	10.57886	5.71166	4.26377	4.53061

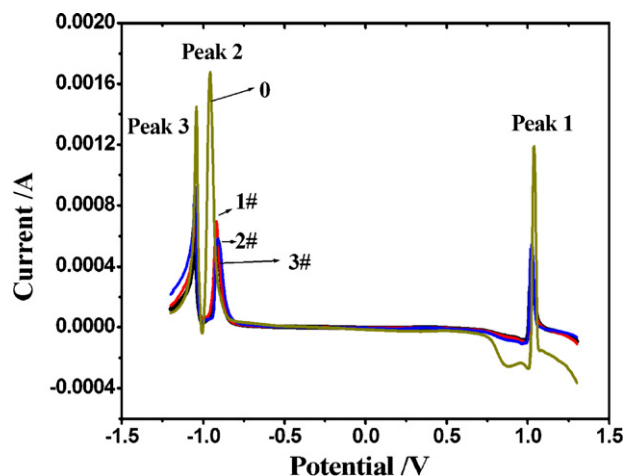


Fig. 3. Linear sweep voltammograms for the anodic films formed on the 0#, 1#, 2# and 3# electrodes oxidized at 1.3 V for 1 h before sweeping the potential to −1.2 V at 1 mV s^{-1} in $1.28 \text{ g cm}^{-3} \text{ H}_2\text{SO}_4$ solution at 25°C .

3.3. Cyclic voltammetry

Fig. 4 shows the cyclic voltammetry curves of the 0#, 1#, 2# and 3# electrodes between −1.7 and 1.7 V in $1.28 \text{ g cm}^{-3} \text{ H}_2\text{SO}_4$ solution with a 5 mV s^{-1} scan rate. **Table 3** provides the peak current and peak potential on the 0#, 1#, 2# and 3# electrodes for the 5th cycle from **Fig. 4**.

Fig. 4 and **Table 3** illustrate that the oxidation and reduction currents on the 1#, 2# and 3# electrodes are significantly lower than those on 0# for the 5th cycle. During the anodic

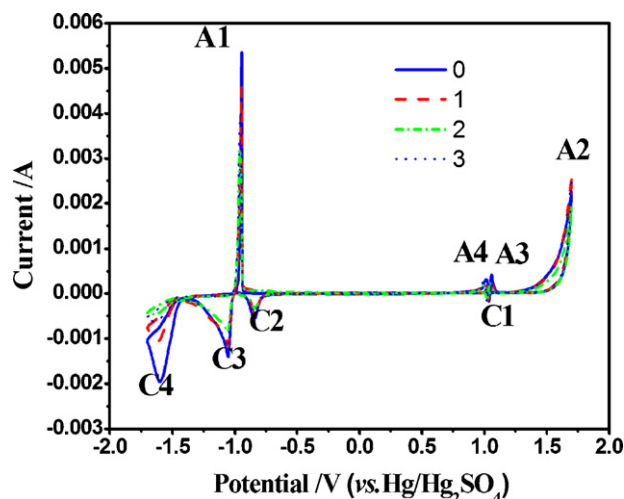


Fig. 4. Cyclic voltammetry curves of the 0#, 1#, 2# and 3# electrodes between −1.7 and 1.7 V for the 5th cycle in $1.28 \text{ g cm}^{-3} \text{ H}_2\text{SO}_4$ solutions at 25°C with a 5 mV s^{-1} scan rate.

potential sweep of the voltammogram, one anodic peak (A1) is observed, corresponding to the formation of lead sulfate. The oxidation current peak A2 is considered as an overlay peak from the transitions of PbSO_4 to PbO_2 and oxygen evolution [14]. In the cathodic potential sweep, four cathodic peaks appeared, which correspond to the transitions of PbO_2 to PbSO_4 (C1) [15], PbO to Pb (C2) [16], PbSO_4 to Pb (C3) [17] and hydrogen evolution (C4), respectively.

It can be seen that two anodic peaks appear clearly on the negative going potential sweep curve (A3 and A4). We suppose that A3 represents the transitions of $\beta\text{-PbO}_2$ to $\alpha\text{-PbO}_2$ and A4 represents the transitions of PbSO_4 to PbO_n [18]. And the negative peak potential shifts resulting from the addition of sodium indicated that this additive can reduce the formation of PbO_n , which is generally thought to have poor conductivity [19].

It can be seen from **Table 3** that the peak current of A1 of the Pb–Na alloys is less than the pure lead electrode, which means the additive can reduce the generation of lead sulfate, hence reduce the anodic electrode corrosion.

Additional cyclic voltammetry, provided in **Fig. 5**, was used to study the electrochemical performance of the Pb and Pb–0.08%Na alloy electrodes between 0.6 and 1.6 V. During the positive sweep, three anodic peaks: peak a, b and c are observed in **Fig. 5**. These correspond to: the oxidation of the alloy substrate to $\alpha\text{-PbO}_2$; the transformation of PbSO_4 to $\beta\text{-PbO}_2$; and the evolution of oxygen, respectively. Meanwhile, a cathodic peak d corresponding to the reduction of PbO_2 appears in the negative sweep [4].

As the number of cycles increases, the reaction currents of oxidation and reduction in cyclic voltammetry of each electrode increase. It is presumed that the increasing peak current can be attributed to the porous corrosion layer formed on the electrode during the cyclic process, which results in a larger true surface area of the corrosion layer. It can clearly be learned from **Fig. 9** that the oxidation and reduction currents for the 5th cycle for Pb–0.08%Na are significantly lower than those for Pb.

Table 3

The peak current and peak potential on the 0#, 1#, 2# and 3# electrodes for the 5th cycle from cyclic voltammetry curves (**Fig. 4**).

Electrode		0#	1#	2#	3#
Peak A1	E_p/V	−0.9498	−0.9516	−0.9516	−0.9534
	I_p/A	0.005524	0.004220	0.002566	0.003389
Peak A2	E_p/V	1.0386	1.2799	1.0244	1.0267
	I_p/A	0.000156	0.000370	0.000066	0.000094
Peak A3	E_p/V	1.0591	1.0504	1.0464	1.0457
	I_p/A	−0.000420	−0.000314	−0.000222	−0.000311
Peak C1	E_p/V	1.0381	1.0261	1.0230	1.0230
	I_p/A	0.000172	0.000262	0.000142	0.000200
Peak A4	E_p/V	1.0193	1.0046	1.0037	1.0010
	I_p/A	−0.000313	−0.000276	−0.000195	−0.000269
Peak C2	E_p/V	−0.8490	−0.8467	−0.8485	−0.8503
	I_p/A	−0.000588	−0.000559	−0.000262	−0.000375
Peak C3	E_p/V	−1.0564	−1.0511	−1.0582	−1.0600
	I_p/A	−0.001410	−0.001072	−0.000725	−0.001015
Peak C4	E_p/V	−1.5978	−1.6170	−1.6298	−1.6291
	I_p/A	0.001959	0.001062	0.000628	0.000458

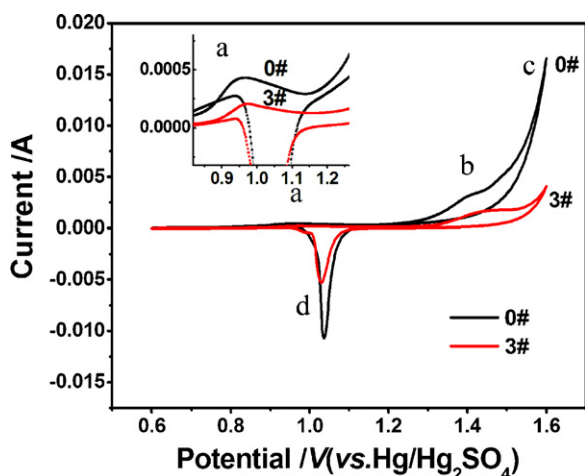


Fig. 5. Cyclic voltammetry curves of Pb and Pb–0.08%Na electrodes between 0.6 and 1.6 V for the 5th cycle in 1.28 g cm^{−3} H₂SO₄ solution with a 5 mV s^{−1} scan rate.

The cathodic reduction charges of the peak d on the Pb and Pb–0.08%Na electrodes in the 5th, 10th, 15th, 20th, 30th, 35th, and 40th cycle are listed in Table 4, and indicate a good linear relationship with the number of cycles.

The cathodic reduction charges of the Pb–0.08%Na are much less than those of lead, which corresponds with the results of LSV experiments between 1.3 and −1.2 V. Based upon these test results, it can be reasonably concluded that the oxidation and corrosion on the Pb electrode are effectively inhibited with the addition of sodium; grid expansion can thereby be decreased, and service life of the grid alloy prolonged.

3.4. Oxygen evolution

LSV experiments were performed to investigate the oxygen evolution behavior of 0#, 1#, 2#, 3# electrodes. The electrodes were oxidized at 1.7 V for 1 h prior to applying a decreasing anodic potential from 1.7 to 1.2 V. The linear sweep voltammograms are illustrated in Fig. 6. Current densities between 1.6 and 1.7 V were selected to construct the Tafel plot. The logarithmic values of current density for the anodic LSV data were calculated and plotted against potential in Fig. 7. The kinetic parameters of the oxygen evolution reaction were determined using linear regression techniques, and are presented in Table 5.

It is observed from Figs. 6 and 7 that the current on each electrode increases with the potential, becoming more positive, and the difference in current density for each electrode becomes more significant with increasing negative potential. The current densities of oxygen evolution on 1#, 2#, 3# electrode are smaller than those on the 0# electrode at the same potential.

Table 5 illustrates the relationship between oxygen evolution potential and the content of sodium, and that the oxygen evolu-

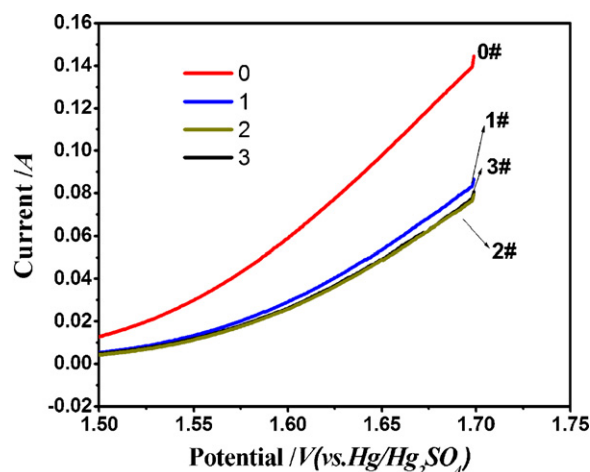


Fig. 6. Linear sweep voltammograms obtained for 0#, 1#, 2#, 3# electrodes with anodic potentials between 1.7 and 1.2 V in 1.28 g cm^{−3} H₂SO₄ solution at 25 °C, at a 1 mV s^{−1} scan rate.

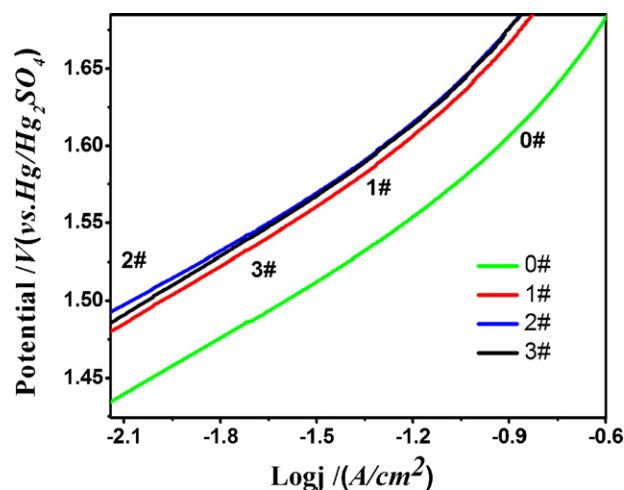


Fig. 7. The Tafel plot obtained on the 0#, 1#, 2# and 3# electrodes for the anodic LSV data.

tion potential of Pb–Na alloys is generally much higher than that of Pb. The addition of sodium to lead can increase oxygen overpotential, consequently suppressing oxygen evolution reaction, which is helpful to prevent water loss and self-discharge, particularly for a sodium content of 0.08%. So Pb–Na alloys are suitable as the positive plate material in lead–acid batteries. We speculate that the inhibition effect was due to extreme reactivity of metallic sodium, which can easily react with the harmful oxygen, thereby reducing oxygen evolution.

3.5. Hydrogen evolution

Additional LSV experiments were performed to investigate the hydrogen evolution behavior of Pb–Na alloys with a cathodic poten-

Table 4

Cathodic reduction charges (Q_c /mC cm^{−2}) of the peak d in the cyclic voltammograms on 0#, 3# electrodes.

Cycles	0#	3#
5	120.22	86.39
10	248.81	138.93
15	337.18	181.13
20	437.9	225.72
25	533.44	264.33
30	617.04	300.96
35	696.66	338.77
40	768.31	374.2
Growth rate (mC cm ^{−2} cycle ^{−1})	18.36	8.12

Table 5

The kinetic parameters of the oxygen evolution reaction obtained from Fig. 7.

Electrode	a (V)	b (V)	R
0#	1.8385	0.2616	0.9968
1#	1.8631	0.2095	0.9966
2#	1.8612	0.2149	0.9971
3#	1.8632	0.2074	0.9966

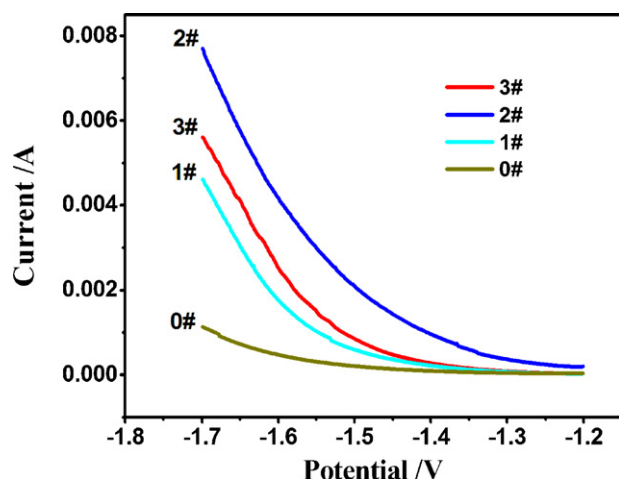


Fig. 8. Linear sweep voltammograms obtained on the 0#, 1#, 2# and 3# electrodes with a cathodic potential range of -1.2 to -1.7 V in 1.28 g cm^{-3} H_2SO_4 solution at 25°C with a 1 mV s^{-1} scan rate.

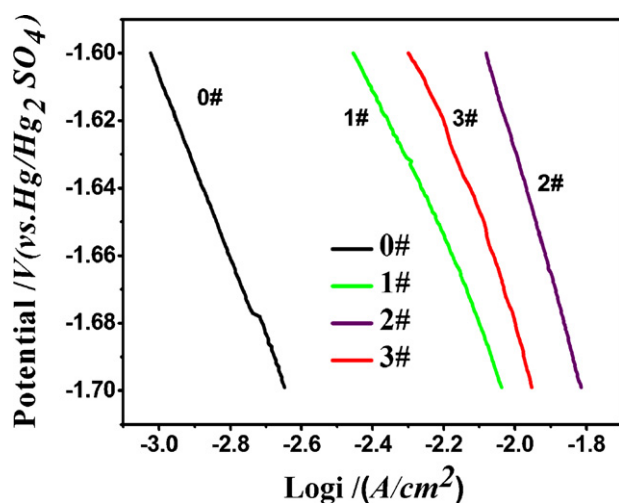


Fig. 9. The Tafel plot obtained for the 0#, 1#, 2# and 3# electrodes from the LSV data.

Table 6

The kinetic parameters of the hydrogen evolution reaction obtained from Fig. 9.

Electrode	a (V)	b (V)	R
0#	-2.3844	-0.2589	-0.9990
1#	-2.1697	-0.2334	-0.9976
2#	-2.3690	-0.3700	-0.9995
3#	-2.2572	-0.2889	-0.9956

tial between -1.2 and -1.7 V, as illustrated in Fig. 8. The logarithmic value of current density from the LSV data was calculated; its correspondence with potential is revealed in Fig. 9. Within a specific range, the relationship between overpotential and current density is described by the Tafel equation:

$$\eta = a + b \times \log|i|$$

in which a and b are the Tafel constants. This equation applies only to the high current density region, thus the region between -1.6 and -1.7 V was selected to construct the Tafel plot. The kinetic parameters of the hydrogen evolution reaction, obtained by linear regression, are presented in Table 6. It illustrates the relationship between the hydrogen evolution potential and the alloy's sodium content.

The hydrogen evolution potential of 1#, 2#, 3# electrodes are more positive than 0#, which means that hydrogen evolution reaction takes place on a Pb–Na electrode more easily than on a Pb electrode, implying that sodium increases hydrogen evolution; this Pb–Na alloy is not, therefore, suitable as a negative grid alloy in lead acid batteries.

4. Conclusions

- 1 The addition of sodium can decrease the generation of Pb(IV) and Pb(II), during the anodic process, and the inhibitory effect of Pb–0.08%Na is the strongest.
- 2 With increasing sodium content, the oxidation and corrosion on the Pb electrode are effectively inhibited; grid expansion can thereby be decreased, and the service life of the grid alloy prolonged.
- 3 The presence of sodium promotes the evolution of hydrogen, yet increases the resistance to oxygen evolution, and this is helpful to prevent water loss and self-discharge occurrence, particularly for a sodium content of 0.08%, suggesting that Pb–Na alloys are suitable as the positive plate material in lead-acid batteries.
- 4 These alloys retain the merits, whilst removing the flaws, of the pure grid, thereby providing a promising new alloy suitable as a positive grid material for spirally wound lead acid batteries.

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